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STUDIES OF COERCIVE FORCE OF PERMANENT MAGNET MATERIALS 1/1
(U) PITTSBURGH UNIV PA DEPT OF CHEMISTRY W E WALLACE
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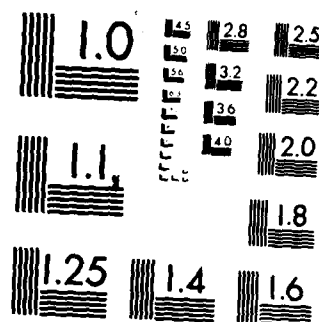
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Permanent magnets were prepared by sintering on-stoichiometry $\text{Sm}_2\text{Co}_{17}$ and $\text{Sm}_2\text{Co}_{17}$ doped with Fe, Mn, Zr and Hf. Coercive forces (iH_c) were low, $< 1 \text{ kOe}$. Although doping increases anisotropy field, it does not enhance iH_c except for Mn as dopant. In this case, doping increases iH_c about two-fold. In these systems iH_c seems to be nucleation-controlled. It is postulated that nucleation occurs at the oxidized surface where anisotropy is weak or negative. Surfaces were investigated by Auger spectroscopy with results consistent with the postulated mechanism. To test for effects of surface roughness, powders were washed with acid. No increase

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In iH_c was observed. Samples ground under pentane and liquid nitrogen showed no significant difference in iH_c . Oxygen content was about 3000 ppm by weight in magnets the finished magnets. Results suggest that coercive force of the so-called 2-17 (which are actually 2-phase mixtures of components with 1:5 and 2:17 stoichiometry) originates with the component having 1:5 stoichiometry.

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Studies of Coercive Force of Rare Earth
Permanent Magnet Materials

by

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FINAL REPORT

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I. Introduction

The so-called 2:17 rare earth-cobalt magnets are actually polycomponent, polyphase systems. Typically these are represented by the formula $\text{Sm}(\text{Co}, \text{Fe}, \text{Mn}, \text{Cu}, \text{Zr})_z$ with z equalling approximately 7.2. The material consists primarily (if not exclusively) of a 1:5 phase and a 2:17 phase. The composition of the phases and the roles of the various components is currently a topic of active inquiry. The origin of the large coercive force of these materials, which gives rise to their high energy product ($> 30 \text{ MGOe}$) is unclear. It is evident that elucidating the mechanism governing coercive force is virtually impossible in such a complex system.

In the present program, on-stoichiometry $\text{Sm}_2\text{Co}_{17}$ together with $\text{Sm}_2(\text{Co}_{1-x}\text{M}_x)_{17}$ ternary alloys have been studied to obtain information in regard to the coercive force of (1) single phase 2:17 stoichiometry materials and (2) the effect of dopants M where $\text{M} = \text{Mn}, \text{Fe}, \text{Zr}$ and Hf . In addition, the effect of acid washes of ball-milled powder and grinding under liquid nitrogen were investigated, the former to remove sharp points and the latter to suppress oxidation. The existence of surface disturbances - sharp points (roughness) - or oxidation facilitates nucleation of inverse domains and hence degrades coercive force.

II. Experimental Results

A. Properties of Pure $\text{Sm}_2\text{Co}_{17}$

This is easily prepared by melting pure Sm and Co together in the proper proportions. High purity Sm obtained from the Ames laboratory was used. The structure of the $\text{Sm}_2\text{Co}_{17}$ was rhombohedral with lattice constants as follows:

	<u>This work</u>	<u>Literature(average)</u>
$a_o(\text{\AA})$	8.402 ± 0.005	8.408 ± 0.03
$c_o(\text{\AA})$	12.216 ± 0.008	12.212 ± 0.024

The room temperature magnetic properties determined were as follows:

Saturation magnetization	113.5 ± 1.5 emu/g, 26.5 ± 0.3 μ_B /f.u.
Anisotropy field	60.0 ± 1.6 kOe
Curie temperature	$920 \pm 2.5^\circ\text{C}$
$4\pi M_{th}$	12.4 kG
$(BH)_{max}$	38.4 MGOe

The intrinsic coercive force (H_c) of $\text{Sm}_2\text{Co}_{17}$ is shown in Figs. 1 and 2. It is dependent upon the time of ball milling and the sintering temperature employed to make the sintered compacts. Ball milling was done under a saturated hydrocarbon. H_c values are seen to be quite small, ranging from < 100 Oe to ~ 650 Oe. These values were not increased by ball milling under liquid nitrogen or by the acid washes. As indicated in the Introduction, liquid nitrogen ball milling was employed in an attempt to reduce oxidation of the material during ball-milling. It is felt that oxidation is deleterious to H_c for reasons set forth below in Section III.

The beneficial effects of increased ball-milling time is ascribed to a better particle size achieved using longer milling times. In samples milled for only 5 hours there were many particles exceeding $10 \mu\text{m}$ in size. These large particles were fewer in number in samples milled for 19 hours. However, in both cases oxidation was extensive. The finished sintermagnets contained ~ 3500 ppm oxygen, about 200-fold greater than in the starting materials.

B. Properties of Doped $\text{Sm}_2\text{Co}_{17}$

In numerous studies from this laboratory, R_2Co_{17} systems have been doped with Cr, Mn, Fe, Ni, Cu, Ti, Zr, Hf and V and studied magnetically.¹⁻¹² Curie temperatures, saturation magnetization and anisotropy fields have been determined as a function of the amount of dopant, i.e., the amount of transition element from the above group which has been substituted for cobalt. It has been found that most of the dopants increase H_A , the anisotropy field. Zr was found to be

the most effective in increasing H_A . One of the features needed in a high energy magnet is a large coercive force. This may or may not develop out of a large H_A . In the present study the effect of dopants Mn, Fe, Zr and Hf on H_c was examined. Results are shown in Figs. 3-5. The data show that Fe, Zr or Hf as substituents have little effect on coercive force, but replacement of Co by Mn (see Fig. 4) sharply enhances coercive force. Thus the special effect of Zr in augmenting H_A does not carry over into an enhanced H_c .

III. Surface Features and Coercive Force

If the Stoner-Wohlfarth coherent rotation model were valid, intrinsic coercive force would be identical with the anisotropy field, H_A . Since H_A is ~ 60 kOe for $\text{Sm}_2\text{Co}_{17}$, H_c via this model would be ~ 60 kOe. Instead (see Figs. 1 and 2), it is 0.1 to 0.3 kOe, smaller by a factor ≥ 200 . Obviously, magnetization reversal takes place more readily than expected by the Stoner-Wohlfarth model. It seems to occur via a nucleation and growth model. Thus, H_c may be controlled either by nucleation or by pinning of domain walls. If nucleation occurs easily, wall pinning will control H_c . It appears that nucleation is very easy for $\text{Sm}_2\text{Co}_{17}$ (and also wall pinning is weak).

The author holds the view that nucleation occurs at or near the surface of $\text{Sm}_2\text{Co}_{17}$. Auger spectroscopy measurements show for this material that the top 30 \AA (~ 10 atom layers) is heavily oxidized. This region, characterized as $\text{Sm}_x\text{Co}_y\text{O}_z$, bears only slight structural resemblance to the limiting cases $\text{Sm}_2\text{Co}_{17}$ (i.e., $x = 2$, $y = 17$, $z = 0$) and Sm_2O_3 (i.e., $x = 2$, $y = 0$, $z = 3$). Sm and Co in these cases will not exhibit their normal single ion anisotropy characteristics,^{13,14} i.e., strongly uniaxial. Instead, as shown by Jin,¹⁵ Sm may exhibit weak uniaxial anisotropy or even planar anisotropy. At these points, nuclei of inverse domains could easily form and then sweep through the sample, giving rise to the low observed coercive force.

Studies on LaCo_5 and PrCo_5 support the ideas advanced in the preceding paragraph. LaCo_5 magnets exhibit H_c of about 9 kOe, whereas PrCo_5 can seldom be formed with H_c greater than 4 kOe. Auger spectroscopy shows that PrCo_5 is more heavily oxidized at the surface than LaCo_5 .

Since oxidation produces the regions where nucleation occurs, it follows that oxidation is deleterious for H_c .

IV. The Coercive Force Mechanism

Ideas expressed in the preceding section, while seeming reasonable, are speculative. In the continuation work supported by the ARO at Carnegie-Mellon University it is hoped to subject these ideas to experimental test. The mechanism governing coercive force of rare earth-cobalt permanent magnet materials is a matter of acute controversy, and the mechanism proposed by the author is just one of the mechanisms proposed.

Some support for the author's ideas is provided by the results obtained for $\text{Sm}_2\text{Co}_{16.5}\text{Mn}_{0.5}$. This is the only ternary for which H_c substantially exceeded that of $\text{Sm}_2\text{Co}_{17}$. Doping with Fe, Hf or Zr left H_c unmodified. In extensive studies of polycrystalline systems containing Mn, it is found that Mn segregates to the surface.¹⁶ If the surface is important for determining H_c , it is to be expected that Mn doping will be effective in modifying H_c .

If coercive force can be understood and controlled, it will be an advance of the first rank in regard to rare earth-cobalt permanent magnet materials. Many materials are known with energy products ≥ 50 MGOe. These energy products could be realized experimentally if $H_c > 13$ kOe could be achieved.

V. Personnel Involved

W. E. Wallace, Principal Investigator
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 F. Pourarian, Research Assistant Professor
 K. Smith, Research Associate
 L. Linck, Secretary
 E. Boltich, Graduate Student

VI. Degrees Earned

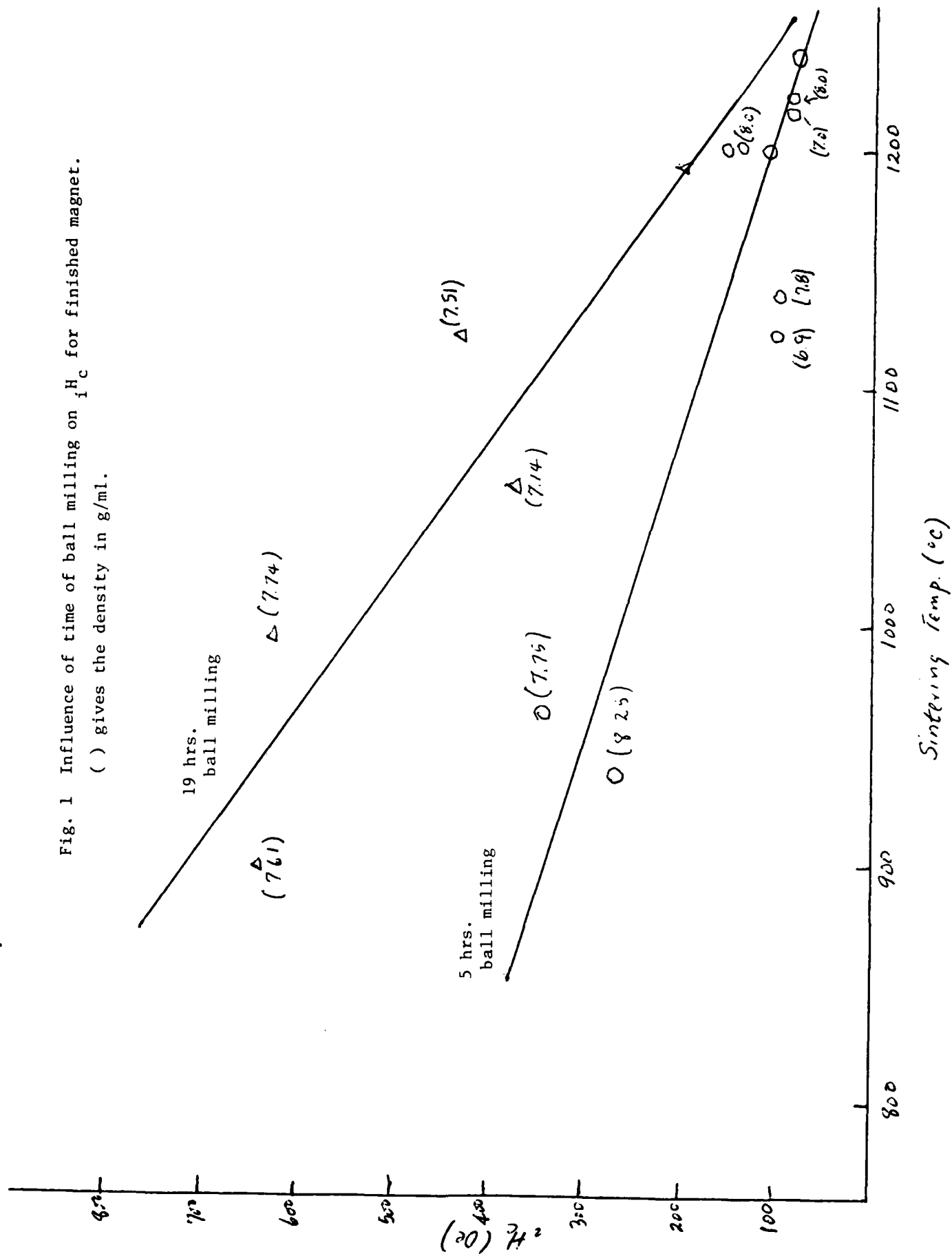
E. Boltich, Ph.D. degree

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Fig. 1 Influence of time of ball milling on H_c for finished magnet.
 () gives the density in g/ml.



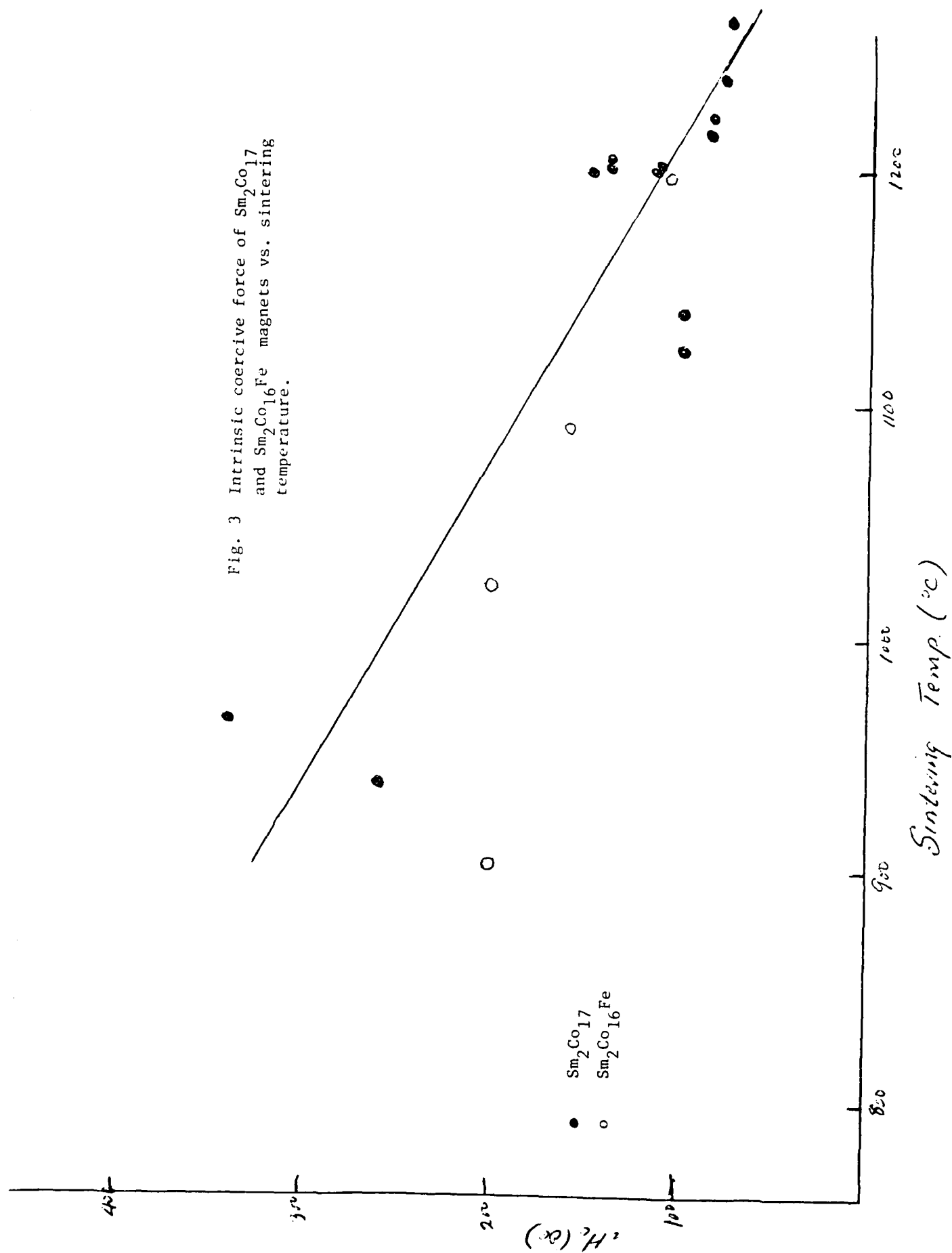


Fig. 4 Intrinsic coercive force of $\text{Sm}_2\text{Co}_{17}$ and $\text{Sm}_2\text{Co}_{16.5}\text{Mn}_{0.5}$ vs. sintering temperature.

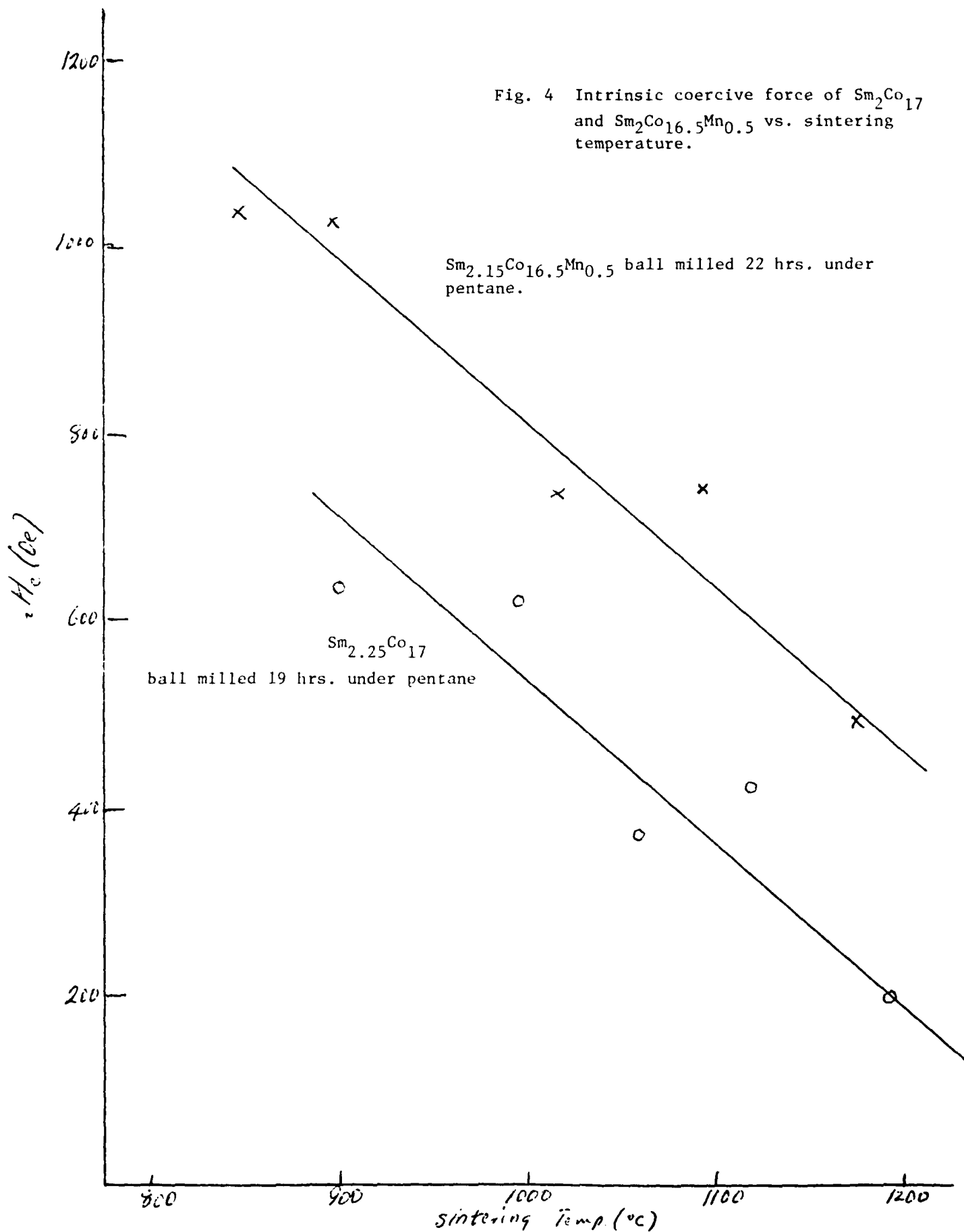


Fig. 5 Intrinsic coercive force of $\text{Sm}_2\text{Co}_{17-x}\text{Zr(Hf)}_x$ magnets versus sintering temperature.
 $\text{Sm}_2\text{Co}_{16.5}\text{Zr}_{0.5}$ (o); $\text{Sm}_2\text{Co}_{16.8}\text{Zr}_{0.2}$ (o);
 $\text{Sm}_2\text{Co}_{16.7}\text{Hf}_{0.3}$ (x).

